The Role of Ni in PtNi Based Nanoparticles for Methanol Oxidation

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The electrooxidation of methanol was studied using Pt, PtNi(1:1 and 3:1), PtRuNi(5:4:1), and PtRu(1:1) alloy nanoparticles in sulfuric acid solution for application to a direct methanol fuel cell, which has numerous advantages such as high theoretical energy density, ease of handling of liquid methanol, and low operating temperatures[1-2]. The PtNi and PtRuNi alloys showed excellent catalytic activities compared to those of pure Pt and PtRu. The role of Ni in the electrocatalytic activity was interrogated using cyclic voltammetry (CV), chronoamperometry (CA), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and X-ray diffraction (XRD). Also unit cell tests of these alloy nanoparticles were performed in order to compare cell performance.

XRD showed alloy formation for all the PtNi, PtRuNi and PtRu nanoparticles since only Pt fcc structures were identified with the diffraction peak shifts from that of pure Pt. The XPS data confirm that the chemical states of Pt are exclusively metal as well as the presence of metallic Ni, NiO, $Ni(OH)_2$, NiOOH, metallic Ru, RuO_2, and RuO_3. Negative shifts of the binding energies of Pt for the PtNi alloy nanoparticles were determined by XPS measurements. This can be explained based by assuming that the enhanced activities of PtNi alloys for methanol electrooxidation were caused by the oxide states of Ni and by the change in the electronic structure of Pt component in the alloys. The difference in peak shifts(figure 1) in Pt 4f XPS between PtNi and PtRu alloy nanoparticles is discussed based on the electronegativity of three components of Pt, Ru, and Ni [3]. In the half cell test of methanol oxidation, the PtRuNi has an excellent catalytic activity, compared with Pt and PtRu, which has the lowest on-set potential of methanol oxidation. Also, the unit cell performance of PtRuNi is superior to that of PtRu as shown in the figure 2. This means that methanol oxidation of PtRuNi nanoparticle is strongly affected by Ni.

References

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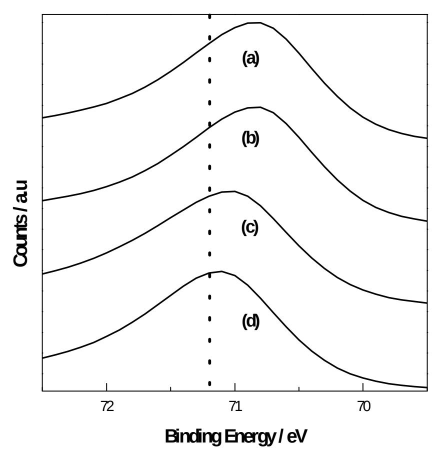

Figure 1. Pt 4f peak shift of Pt nanoprticles; (a) PtNi(1:1), (b) PtNi(3:1), (c) PtRuNi(5:4:1), and (d) PtRu(1:1)

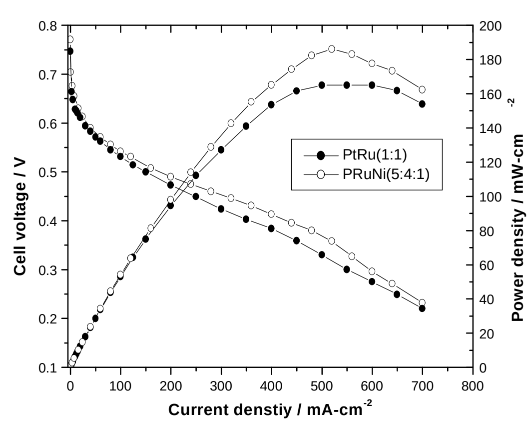

Figure 2. The comparisons of cell performance in PtRuNi(5:4:1) and PtRu(1:1).